

# Perturbation Theory on Top of Optimized Effective Potential Method

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We present a perturbative approach within the scope of Kohn-Sham density functional theory (DFT). The method is based on the exact exchange-only optimized effective potential method, and correlation is included via perturbation expansion using Rayleigh-Schrödinger (RS) perturbation theory (PT). The correlation potential is constructed from Møller-Plesset formulation of RS calculations. This naturally leads to a new iterative scheme when finite order perturbation theory is employed. The new iterative procedure can be taken as a self-consistent parameter-free DFT PT, and, as such, provides correlation energy which is explicitly functional of the self-consistent orbitals, eigenvalues and also of the exchange-correlation potential. As a demonstration, terms up to the second order in the PT expansion are considered and the explicit formula for the second order correlation potential is given as well.

## I. INTRODUCTION

Kohn-Sham (KS) density functional theory (DFT) is a formally exact treatment of the many-body problem [1]. Kohn and his co-workers showed that the exact equations of quantum mechanics, taking into account all the electrons in a molecule (or solid) can be replaced by simpler equations in which only the density of electrons at each point in space enters [1]. Remarkable success has been achieved in the last decades in finding the "missing link" of KS-DFT, the accurate exchange-correlation energy functional  $E_{xc}[\rho]$ . The possibility of further improvements of model functionals, however, seems to be rather limited within the scope of the so-called second generation of DFT, in which the kinetic energy is expressed in terms of orbitals, while the exchange-correlation energy  $E_{xc}$  as an electron density functional. Furthermore, "state-of-the art" exchange-correlation energy functionals  $E_{xc}[\rho]$  and potentials  $v_{xc}(\mathbf{r})$ , such as the generalized gradient approximation (GGA) [2] suffer from serious problems since they do not exhibit the correct  $-\frac{1}{r}$  long-range and quadratic behaviour at small  $r$  [3,4]. It became also apparent that GGA is not able to reproduce exchange-correlation energies and potentials simultaneously with the accuracy provided by the energy functionals [4]. All this indicates that although density gradient treatments have had some success, they are not sufficiently well developed at present to provide a final answer to the problem of determining the exchange-correlation

contribution to the ground-state energy functional or to the one-body potential [5].

A new generation of DFT, the optimized effective potential method (OEP) [6,7], opens a new horizon towards fully local and exact mean-field theory, where not only the kinetic energy but also the exchange-correlation potential and the exchange-correlation energy are treated at the orbital dependent level of theory. The efficient and highly accurate KLI approximation to OEP provides an efficient computational tool for the scientific community. OEP and KLI build up correct  $-\frac{1}{r}$  asymptotics and the highest occupied orbital energy satisfies Koopmans-theorem and also provides self-interaction free exchange-correlation potential  $v_{xc}(\mathbf{r})$  [3]. However, the theory is exact at the exchange-only level and electron correlation can only be added via approximate correlation energy functionals [8]. It must be emphasized that the correlation energy functionals neither in their local nor in gradient corrected form are likely to work in combination with exact exchange. This is because basically none of the common correlation functionals have a long-range component in the corresponding correlation hole (the combined exchange-correlation hole is typically short-ranged). The Colle-Salvetti gradient corrected correlation functional [9], which provided excellent results for atoms, performed rather badly for molecules due to the abovementioned reason [8]. Approximate correlation functionals, which are derived from the homogeneous or inhomogeneous electron gas model or obtained non-empirically from sum-rule conditions, exhibit incorrect long-range tail (only dynamical correlation is accounted for). Those functionals also build up improper local behaviour in atoms and molecules and their success is mainly due to the cancellation of errors with different sign [4,10]. Therefore, the correlation effect can only be calculated in a more complicated way than in the second generation of DFT in those methods which work with exact exchange (e.g. HF and OEP) [20].

A few extensions of the OEP method have been made, which allow the treatment of electron correlation in a limited way. In recent years much effort has been devoted to the formulation of perturbation theory (PT) on KS basis. Recently Rayleigh-Schrödinger PT has been employed for the DFT correlation energy using explicit coupling-constant dependence in the model Hamiltonian within the KS density functional picture [11]. The Görling-Levy scheme and OEP provide the exact treatment of the exchange-only KS problem and also provide an alternative to the Hartree-Fock theory. Casida, on the other

hand, employed an approximate perturbative expression for the ground state to include correlation in OEP [12] using a formalism based on the work of Sham and Schlüter [13]. In a recent review of OEP, Grabo *et al.* proposed a scheme which also makes use of many-body perturbation theory (MBPT) on exchange-only OEP reference state using Green's functions and the Dyson equation [14]. Very recently, Engel *et al.* worked out the relativistic generalization of OEP and used Møller-Plesset based correlation [15]. Aashamar *et al.* gave the extension of OEP approach which, permits the treatment of correlation in a limited way at the multiconfigurational self-consistent field (MCSCF) level of theory [17]. However, this approach met little practical relevance being extremely time-consuming and also difficult to relate to the single determinant nature of KS DFT.

The density functional perturbation theory worked out by X. Gonze *et al.* [18], which can be taken as a variation-perturbation procedure. In this as well as in other theories [11] the self-consistent procedure led to the Kohn-Sham wave function being dependent on the perturbation theory. Thus the perturbation comes into play at an earlier stage than in conventional quantum chemical perturbation theory (e.g. Møller-Plesset perturbation theory). Also, Holas and March expressed the exact exchange-correlation potential in terms of first- and second order density matrices using the Görling-Levy perturbation theory [19]. All these methods appear somewhat complex in detail and it is presently difficult to predict which one will prove the most convenient for practical application and implementation [19].

The Kohn-Sham formalism for ground states is based on the noninteracting Schrödinger equation

$$[\hat{T} + \hat{v}_s]\Phi = E_s^{KS}\Phi, \quad (1)$$

the KS equation, where  $\hat{v}_s$  is the  $N$ -electron operator which corresponds to a local multiplicative potential  $v_s(\mathbf{r})$  as a consequence of the Hohenberg-Kohn theorem [1]. The one-body KS potential  $v_s(\mathbf{r})$  is determined, up to an additive constant, by the requirement that the ground state of the KS Hamiltonian operator  $\hat{T} + \hat{v}_s$ , the KS wave function  $\Phi$ , yields the same electron density  $\rho(\mathbf{r})$  as the ground state of the corresponding interacting real system.  $\Phi$  can be composed of  $N$  spin orbitals  $u_i$  as a single Slater determinant for nondegenerate systems. Therefore, the following spinrestricted Kohn-Sham single-particle approach is considered for fermionic systems (we have omitted spin-dependency, but the extension of the theory is straightforward for that case, throughout a.u. is used):

$$[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})]u_i(\mathbf{r}) = \epsilon_i u_i(\mathbf{r}) \quad (2)$$

where  $u_i(\mathbf{r})$  and  $\epsilon_i$  are the single particle orbitals and eigenvalues for a fermionic system and  $v_s(\mathbf{r})$  is the effective Kohn-Sham single particle potential [1].

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}), \quad (3)$$

where  $v_{ext}$  is the potential external to the electronic system that includes the one created by nuclei,  $v_H$  is the Coulomb potential due to the classical electron-electron repulsion and  $v_{xc}$  is a nonclassical term, the exchange-correlation contribution to the the KS one-body potential.

In this article we would like to study a more general class of KS potentials. In a general sense, the exchange-correlation part of the KS potential is not a pure density functional but rather a complicated functional of eigenvalues and of single particle orbitals [20],

$$\begin{aligned} v_s([\rho], \mathbf{r}) &= v_s([\rho], \{u_i\}, \{\epsilon_i\}, \mathbf{r}) \\ &= v_{ext}([\rho], \mathbf{r}) + v_H([\rho], \mathbf{r}) \\ &\quad + v_{xc}([\rho], \{u_i\}, \{\epsilon_i\}, \mathbf{r}) \end{aligned} \quad (4)$$

In addition to this, in the section V we will show that the exchange-correlation energy  $E_{xc}$  is even more complicated energy functional being the explicit functional of the exchange-correlation potential  $v_{xc}(\mathbf{r})$  as well,

$$E_{xc} = E_{xc}[\{u_i, \epsilon_i\}, v_{xc}]. \quad (5)$$

The same conclusion is derived by others [14]. As demonstrated by Görling and Levy [11], it is not necessarily important to know how the exchange-correlation potential, based on the eigensolutions of the KS equations, depends on the density. Those potentials are always implicitly functionals of the density.

To derive  $v_{xc}$  formally, we write  $E_{xc}$  rigorously

$$E_{xc}[\rho] = \frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r}' d\mathbf{r} \frac{\rho(\mathbf{r})\rho(\mathbf{r}') [g^\lambda([\rho]; \mathbf{r}, \mathbf{r}') - 1]}{|\mathbf{r} - \mathbf{r}'|}, \quad (6)$$

where  $g^\lambda([\rho]; \mathbf{r}, \mathbf{r}')$  can be interpreted as the pair correlation function of the fictitious system with interaction strength parameter (coupling constant)  $0 \leq \lambda \leq 1$  and a ground state density which is independent of  $\lambda$  [1,4]. The exchange-correlation potential  $v_{xc}$  is formally defined as the functional derivative

$$v_{xc}(\mathbf{r}, [\rho]) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. \quad (7)$$

Because of the Hohenberg-Kohn theorem, there exists a one-to-one mapping between the single particle KS potentials  $v_s(\mathbf{r})$  and the densities  $\rho(\mathbf{r})$  which guarantees that the functional derivative given by Eq. (7) is defined [1]. However, the functional derivation can not be obtained explicitly, since one has to derive the following expression [4]:

$$\begin{aligned} v_{xc}(\mathbf{r}, [\rho]) &= \int_0^1 d\lambda \left\{ \int d\mathbf{r}' \frac{\rho(\mathbf{r}') [g^\lambda([\rho]; \mathbf{r}, \mathbf{r}') - 1]}{|\mathbf{r} - \mathbf{r}'|} + \right. \\ &\quad \left. \frac{1}{2} \int d\mathbf{r}' d\mathbf{r}'' \frac{\rho(\mathbf{r}')\rho(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} \frac{\delta g^\lambda([\rho]; \mathbf{r}', \mathbf{r}'')}{\delta \rho(\mathbf{r})} \right\}. \end{aligned} \quad (8)$$

The first term of the potential is the so-called *potential* part of the exchange-correlation energy [4], which is identical with Slater's potential in the exchange-only (x-only) case, i.e. for  $g^\lambda$  approximated by  $g^{\lambda=0}$ , and which is exactly known [23] as an orbital dependent quantity. The *response* like second term contains the fundamental functional derivative of the pair correlation function which is, however, an unknown functional. The functional derivative Eq. (7) can be calculated only for approximate functionals analitically where explicit dependence on the density  $\rho$  is known and therefore to be applied only for the so-called second generation of DFT [14]. In the third generation of DFT one uses  $E_x[\{u_i\}]$  rather than  $E_x[\rho]$  so that not only the kinetic energy but the exchange energy is expressed as orbital dependent energy functionals. The correlation energy must be determined, though as a density functional [4,14]. The central equation in the third generation of DFT is still the KS Eq. (2) [20,14]. At the best of our knowledge attempts have not yet been made to express the exchange-correlation energy as a unique orbital-dependent quantity  $E_{xc}[\{u_i\}]$  in OEP. Furthermore, a general theory to be set up, where both the exchange-correlation potential and the energy are complicated functionals of the self-consistent solutions of the eigenvalue problem Eq. (2) in the spirit of Eqs. (3) and (4).

In this work we give an explicit formulation of a perturbation theory on top of exchange-only OEP. We derived an explicit expression for the correlation potential given by Krieger *et al.* [3]. In section II, we give the short summary of OEP formalism, which we use extensively in the further sections of this article. We give in sections III-IV, the potential and response part of  $v_{xc}$  (see Eq. (7)) exactly. We formulate a self-consistent perturbation theory on top of the exchange-only OEP reference state (section V). We would also like to compare our OEP-PT scheme with other DFT schemes obtained by perturbation theory [11,15] in order to point out the similarities and differences between them.

## II. OPTIMIZED EFFECTIVE POTENTIAL METHOD

The starting point of the OEP method is the total energy functional

$$E_{tot}^{OEP}[\{u_i\}] = \sum_{i=1}^{occ} \int d\mathbf{r} u_i^*(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 \right) u_i(\mathbf{r}) + \int d\mathbf{r} \rho(\mathbf{r}) v_{ext}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}^{OEP}[\{u_i\}], \quad (9)$$

where, in contrast with ordinary DFT, the exchange-correlation energy is an explicit functional of orbitals, and, therefore, only implicit functional of the density via Eqs. (2)-(3) [3,14].  $i$  is a collective index for all orbital

quantum numbers. The local single-particle potential appearing in Eqs. (2)-(3) must be the optimized one yielding orbitals which minimize  $E_{tot}^{OEP}[\{u_i\}]$  so that

$$\left. \frac{\delta E_{tot}^{OEP}[\{u_i\}]}{\delta v_s(\mathbf{r})} \right|_{v_s=v^{OEP}} = 0. \quad (10)$$

As first pointed out by Perdew and co-workers, Eq. (10) is equivalent to the Hohenberg-Kohn variational principle [14,22].

The optimized effective potential method (OEP) is given by Talman and Shadwick [7] for getting the exact exchange potential  $v_x(\mathbf{r})$ . Formally, we make use of chain rule for the functional derivative Eq. (6) to obtain

$$v_{xc}^{OEP}(\mathbf{r}, [\rho]) = \frac{\delta E_{xc}[\{u_i[\rho]\}]}{\delta \rho(\mathbf{r})} = \sum_{i=1}^{occ} \int d\mathbf{r}' \frac{\delta E_{xc}^{OEP}[\{u_i\}]}{\delta u_i(\mathbf{r}')} \frac{\delta u_i(\mathbf{r}')}{\delta \rho(\mathbf{r})} + c.c. \quad (11)$$

where  $\{u_i[\rho]\}$  are the orbitals which are, however, implicitly functionals of the density. Applying the functional chain rule again and after some algebra one can get the following integral equation [3,11,24]:

$$\sum_i u_i(\mathbf{r}) \int d\mathbf{r}' [v_{xc}^{OEP}(\mathbf{r}') - v_i(\mathbf{r}')] G_i(\mathbf{r}, \mathbf{r}') u_i^*(\mathbf{r}') + c.c. = 0 \quad (12)$$

where

$$v_i(\mathbf{r}) = \frac{1}{u_i^*(\mathbf{r})} \frac{\delta E_{xc}[\{u_i\}]}{\delta u_i(\mathbf{r})}, \quad (13)$$

and  $G_i(\mathbf{r}, \mathbf{r}')$  is the Greens function

$$G_i(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i} \frac{u_j^*(\mathbf{r}) u_j(\mathbf{r}')}{\epsilon_j - \epsilon_i}, \quad (14)$$

The integral Eq. (12) is the fundamental expression for  $v_{xc}$  in OEP instead of Eq. (7), however, there is no known analytic form of  $v_{xc}[\{u_i\}]$ . Therefore, only numerical solutions are available for spherical atoms [3,7,14,16,17] and for solids [25–27]. These numerical solutions of Eq. (12) are confined to the exchange-only OEP and correlation has been taken into account only via approximate local functionals [25]. At the best of our knowledge, the only possibility to account for the correlation energy exactly is the constrained search formulation of KS theory, when one makes use of fully correlated density as a reference density obtained from e.g. full CI calculations [4,10]. Although such a calculation provides exact  $v_{xc}$ , it represents an enormous computational task which can hardly be carried out for systems of practical interest. Görling and Levy have pointed out that Eq. (12) is the special case of a more general equation [28].

In the work of Krieger and co-workers, the OEP integral equation is analyzed and a simple approximation is

made reducing the complexity of the original OEP equation significantly, and, at the same time, keeping many of the essential properties of OEP unchanged [3]. Krieger, Li and Iafrate gave an exact expression by transforming the OEP integral Eq. (7) into a manageable form. They have got the following, still *exact* expression for  $v_{xc}(\mathbf{r})$ :

$$v_{xc}^{OEP}(\mathbf{r}) = v_{xc}^S(\mathbf{r}) + \sum_i^{occ} \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})} (\bar{v}_{xci}^{OEP} - \bar{v}_i) + \frac{1}{2} \sum_i^{occ} \frac{\nabla[p_i(\mathbf{r})\nabla u_i(\mathbf{r})]}{\rho(\mathbf{r})}, \quad (15)$$

where  $v_{xc}^S(\mathbf{r})$  is the Slater's potential given as the first term in Eq. (7) in exchange-only case. However, Slater's potential can be generalized to include the potential part of the correlation energy density as well [3,4]. The exchange component of  $v_{xc}^S$

$$v_x^S(\mathbf{r}) = -\frac{1}{2\rho(\mathbf{r})} \sum_{i,j}^{occ} u_i(\mathbf{r})u_j^*(\mathbf{r}) \int d\mathbf{r}' \frac{u_i^*(\mathbf{r}')u_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \quad (16)$$

The summation runs over the orbital index for all the occupied orbitals up to the highest occupied  $m$ th orbital (Fermi level). The function  $p_i(\mathbf{r})$  is defined by

$$p_i(\mathbf{r}) = \frac{1}{u_i(\mathbf{r})} \int d\mathbf{r}' [v_{xc}^{OEP}(\mathbf{r}') - v_i(\mathbf{r}')] G_i(\mathbf{r}, \mathbf{r}') u_i(\mathbf{r}'), \quad (17)$$

with the partial density  $\rho_i(\mathbf{r}) = u_i^*(\mathbf{r})u_i(\mathbf{r})$ . In practical applications the last term in Eq. (15) turns out to be quite small in atomic systems and has a small effect only on the atomic shell boundaries [3]. The neglect of this term then leads to the KLI-approximation which has the following form after some algebra [3].

$$v_{xc}^{KLI}(\mathbf{r}) = v_{xc}^S(\mathbf{r}) + \sum_{i=1}^{m-1} \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})} \sum_{j=1}^{m-1} (\mathbf{A}^{-1})_{ij} (\bar{v}_{xcj}^S - \bar{v}_j). \quad (18)$$

$$\sum_{j=1}^{m-1} (\mathbf{A}^{-1})_{ij} (\bar{v}_{xcj}^S - \bar{v}_j) = \bar{v}_{xci}^{KLI} - \bar{v}_i,$$

$$\mathbf{A}_{ji} = \delta_{ji} - \mathbf{M}_{ji},$$

$$\mathbf{M}_{ji} = \int \frac{\rho_j(\mathbf{r})\rho_i(\mathbf{r})}{\rho(\mathbf{r})} d\mathbf{r}, i, j = 1, \dots, m-1$$

$$v_{xc}^S(\mathbf{r}) = \sum_{i=1}^m \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})} v_i(\mathbf{r}),$$

$$\bar{v}_j^S = \int d\mathbf{r} \rho_j(\mathbf{r}) v_{xc}^S(\mathbf{r})$$

$$\bar{v}_{xcj} = \bar{v}_{xj}^{HF} + \int d\mathbf{r} \rho_j(\mathbf{r}) v_{xcj}(\mathbf{r}).$$

$$\bar{v}_{xj}^{HF} = -\frac{1}{4} \sum_{i=1}^{occ} \int d\mathbf{r} d\mathbf{r}' \frac{u_i(\mathbf{r})u_j^*(\mathbf{r}')u_i^*(\mathbf{r}')u_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}, \quad (19)$$

where  $m$  is the Fermi level (the highest occupied one-electron energy level) and note that the  $m$ th level is excluded because  $\bar{v}_m^{KLI} = \bar{v}_m^{HF}$  [3]. This might appear a rather crude approximation, but it can be interpreted as a mean-field approximation since the neglected terms averaged over ground-state density vanish. It can be shown that the KLI approximation can be derived alternatively [21].

### III. PERTURBATION EXPANSION OF THE CORRELATION ENERGY ON TOP OF EXCHANGE-ONLY OEP

Let us turn now to the discussion of how to include electron correlation on top of exact exchange-only KS theory. Our aim is to solve the exact KS scheme using perturbation theory on top of a known first order problem (e.g. the x-only OEP). Here consider the Hamiltonian for an  $N$ -electron system

$$\hat{\mathbf{H}} = \hat{\mathbf{T}} + \hat{\mathbf{V}}_{ee} + \sum_{i=1}^N v_{ext}(\mathbf{r}_i), \quad (20)$$

where  $\hat{\mathbf{T}} = \sum_{i=1}^N -\frac{1}{2}\nabla_i^2$ ,  $\hat{\mathbf{V}}_{ee} = V_{ee}(\mathbf{r})$  stands for the electron repulsion as a local operator and  $v_{ext}(\mathbf{r}_i)$  is the external (nuclear) potential of the nuclear frame.

We consider the problem of improving the exchange-only OEP energy of an  $N$ -electron system by means of Rayleigh-Schrödinger (RS) perturbation theory. The partition of the Hamiltonian is defined  $\mathbf{H}$  as

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{W} \quad (21)$$

In particular, we treat  $\mathbf{W}$  as a perturbation to the *exchange-only* KS Hamiltonian  $\mathbf{H}_0$  ( $\mathbf{H}_0 \gg \mathbf{W}$ ). We wish to solve the eigenvalue problem

$$\hat{\mathbf{H}}\Phi = (\hat{\mathbf{H}}_0 + \hat{\mathbf{W}})\Phi = E\Phi, \quad (22)$$

which leads to a non-degenerate ground state for a system of  $N$ -fermions.  $\Phi$  is the ground state wavefunction and  $E$  is the expectation value of the Hamiltonian given by Eq. (20) and (21). Eq. (22) describes the corresponding KS system, a model system of hypothetical noninteracting electrons with the same ground-state electron density

as the real system [1,5,11]. However, we only know the solution of the unperturbed problem

$$\hat{\mathbf{H}}_0 \Phi_s = E_0 \Phi_s, \quad (23)$$

where  $\hat{\mathbf{H}}_0, \Phi_s$  are the unperturbed reference Hamiltonian and single determinant wavefunction. We assume that Eq. (23) provides a complete set of eigenfunctions  $\{u_i\}$  with corresponding eigenvalues  $\{\epsilon_i\}$  as well as the nondegenerate ground energy state  $E_0$ . In this article we treat  $\mathbf{H}_0$  as the exact exchange-only KS Hamiltonian, which is known as the exchange-only OEP Hamiltonian. Actually, the solutions of exact x-only OEP are equivalent to the solutions of the exact x-only KS equations [14]. The central idea is now to determine the perturbation operator  $\hat{\mathbf{W}}$  as a functional derivative with respect to the electron density  $\rho$  (Eq. (7)).

$$\begin{aligned} \hat{\mathbf{W}} = W(\mathbf{r}) &= \frac{\delta(E - \langle \Phi_s | \hat{\mathbf{H}}_0 | \Phi_s \rangle)}{\delta \rho} \\ &= \hat{V}_{ee}(\mathbf{r}) - v_H(\mathbf{r}) - v_x(\mathbf{r}). \end{aligned} \quad (24)$$

Therefore, the perturbation operator  $\hat{\mathbf{W}}$  is treated as a local potential  $W(\mathbf{r})$ . The calculated operator  $\hat{\mathbf{W}}$  can be then substituted back to the Hamiltonian given by Eq. (21) and the eigenvalue problem (Eq. (22)) can be solved. The unknown ground state energy  $E$  in Eq. (24) is expressed by RS perturbation theory. In section V we give the details of this iterative scheme, in particular when the reference state is the exchange-only OEP method.

We treat  $v_s([\rho]; \mathbf{r})$  in this article as an explicit functional of the eigensolutions  $\{u_i, \epsilon_i\}$  of the single particle Hamiltonian (to be interpreted as the KS one). Therefore, the unknown potential  $v_{xc}$  is implicit functional of the ground state density according to the Hohenberg-Kohn theorem [1]. Its uniqueness is also guaranteed by the Hohenberg-Kohn theorem.  $v_s([\rho]; \mathbf{r})$  in Eq. (2) is a one-body operator and Eq. (23) reduces to one-particle equations for KS single particle orbitals  $u_i(\mathbf{r})$  as given by the noninteracting one-particle Schrödinger Eq. (2) with the exact x-only KS one-body operator  $v_s^{xOEP}$ . The KS single determinant,  $\Phi_s$ , in Eq. (23) is then formed from all occupied one-particle KS orbitals,  $\{u_i\}$ , i.e., the  $N$  energetically lowest solutions to Eq. (23) with  $N$  being the number of electrons in the system of interest. Eq. (22) reduces to exact one-particle KS equations given by Eq. (2) with the exact KS one-body operator  $v_s(\mathbf{r})$ . Furthermore, the one-body potentials, which correspond to the x-only reference state ( $v_s^{xOEP}$ ) as well as to the exact (correlated) case ( $v_s^{KS}$ ) together with the Hamiltonians  $\mathbf{H}_0$  and  $\mathbf{H}$ , are unique functionals of the  $v$ -representable density. However, it must be emphasized that the x-only OEP will result in ground state density different from the exact KS scheme given in Eq. (22).

The functional derivation given by Eq. (24) can not be carried out directly due to the difficulties given in Eqs. (7)-(8). The derivative is directly not accessible since  $E_{xc}$

is known only in terms of the one-particle KS states  $\{u_i\}$  and the eigenvalues  $\{\epsilon_i\}$ , and the explicit functional dependence of the KS eigensolutions on the electron density is unknown. OEP provides an alternative way of getting the local operator  $\hat{\mathbf{W}}(\mathbf{r})$ . The solution of Eq. (23) is identical with the solution of Eq. (12) for exchange-only OEP. Therefore, we chose the following partition of  $\mathbf{H}$  according to Eq. (22),

$$\mathbf{H}_0 = \sum_i (h_i + \hat{v}_i^{OEP}) \quad (25)$$

and

$$\mathbf{W}(\mathbf{r}) = \hat{V}_{ee}(\mathbf{r}) - \sum_i \hat{v}_i^{OEP}(\mathbf{r}), \quad (26)$$

where  $h_i$  is the one-electronic Hamiltonian which contains the kinetic operator and the operator of the external (nuclear) potential ( $\hat{h}_i = \hat{t}_i + v_{ext}(\mathbf{r}_i)$ ).  $\hat{V}_{ee}$  stands for the electron-electron repulsion as a local operator. The exchange component of the perturbed operator is taken into account by

$$\hat{v}^{OEP}(\mathbf{r}) = \sum_{i=1}^{occ} \hat{v}_i^{OEP}(\mathbf{r}) = \sum_i^{occ} [\hat{j}_i(\mathbf{r}) - \hat{k}_i(\mathbf{r})], \quad (27)$$

where  $v_H(\mathbf{r}) = \sum_i^{occ} \hat{j}_i(\mathbf{r})$  and  $\hat{k}_i(\mathbf{r})$  are the corresponding local Coulomb and exchange operators.  $\hat{k}_i(\mathbf{r})$  is given according to Eq. (15), where  $v_x^{OEP}(\mathbf{r}) = \sum_{i=1}^{occ} \hat{k}_i(\mathbf{r})$ . The partition of the Hamiltonian given above can be taken as an operator for Møller-Plesset (MP) perturbation expansion [29,30] employed on orbitals and obtained by the solution of x-only OEP equations.

The exchange-only OEP total energy  $E_{tot}^{xOEP}$  can be considered as the sum of zeroth and first-order energies,

$$\begin{aligned} E_{tot}^{xOEP} &= E^{(0)} + E^{(1)} = \sum_i^{occ} \epsilon_i - \langle \Phi_s | \hat{\mathbf{W}} | \Phi_s \rangle \\ &= \sum_i^{occ} \epsilon_i - E_x^{OEP}[\{u_i\}], \end{aligned} \quad (28)$$

where

$$E_x^{OEP}[\{u_i\}] = -\frac{1}{4} \sum_{ij}^{occ} \int d\mathbf{r} d\mathbf{r}' \frac{u_i(\mathbf{r}) u_j^*(\mathbf{r}) u_i^*(\mathbf{r}') u_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (29)$$

According to Eq. (9) the exact (correlation corrected) total energy  $E_{tot}^{(n),OEP}$  can be given at the  $n$ th order level of perturbation theory

$$E_{tot}^{(n),OEP}[\{u_i\}] = E_{tot}^{xOEP} + E_c^{(n \geq 2)}. \quad (30)$$

The first correction to the exchange-only energy occurs in the second order of perturbation theory.

The correlation energy is expanded as the sum of correlation contributions at any order, so that

$$E_c^{(n)}[\{u_i, \epsilon_i\}] = \sum_{p=2}^n \varepsilon^p[\{u_i, \epsilon_i\}]. \quad (31)$$

Next step is to express the unknown correlation potential in order to solve the correlated KS problem given by Eq. (22). The correlation potential is also determined according to the perturbation theory at  $n$ th order level of theory keeping in mind that correlation and exchange effects are decomposed,

$$v_{xc}(\mathbf{r}) = v_x(\mathbf{r}) + v_c^{(n)}(\mathbf{r}). \quad (32)$$

For  $v_c$  we employ the expression, obtained from the exact transformation of the OEP integral Eq. (12) and given by Eq. (15). For sake of simplicity, however, we use the remarkably accurate KLI approximation, and neglect the rather difficult last term in Eq. (15). According to Eq. (18)  $v_c^{(n)}$  can then be written

$$v_c^{(n)}(\mathbf{r}) = v_c^{S(n)}(\mathbf{r}) + \sum_{ij}^{m-1} \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})} \mathbf{A}_{ij}^{-1} (\bar{v}_{cj}^{S(n)} - \bar{v}_{cj}^{(n)}). \quad (33)$$

We would like to note here that none of the existing DFT-PT schemes [11,15,18] used directly this OEP expression for the correlation potential. Instead they derived the correlation potential in an alternative way. Görling and Levy employed functional derivation over the second order correlation energy with respect to the Kohn-Sham potential and to the eigenvalues. Engel *et al.* also applied the GL PT over the relativistic OEP leading to functional derivations with respect to the KS orbitals and to the KS eigenvalues. Both theories will lead to different expressions. We use, however, functional derivation with respect to only the orbitals according to Eq. (13). In the next few steps and in the next section we will show that this difference will lead naturally to different correlation potential then those given by the authors mentioned above. This formulation of the correlation potential has *Slater* and *response* component [4,3],

$$v_c^{(n)}(\mathbf{r}) = v_c^{S(n)}(\mathbf{r}) + v_c^{resp,(n)}(\mathbf{r}), \quad (34)$$

and can be extracted as follows,

$$v_c^{S(n)}(\mathbf{r}) = \sum_{j=1}^{occ} \frac{\rho_j(\mathbf{r})}{\rho(\mathbf{r})} v_{cj}^{(n)}(\mathbf{r}), \quad (35)$$

$$\bar{v}_{cj}^{S(n)} = \int d\mathbf{r} \rho_j(\mathbf{r}) v_c^{S(n)}(\mathbf{r}), \quad (36)$$

$$\bar{v}_{cj}^{(n)} = \int d\mathbf{r} \rho_j(\mathbf{r}) v_{cj}^{(n)}(\mathbf{r}), \quad (37)$$

The  $n$ th-order orbital dependent potential  $v_{cj}^{(n)}$  can be given using the Møller-Plesset correlation energy  $E_c^{(n)}$  given in Eq. (31)

$$v_{cj}^{(n)}(\mathbf{r}) = \frac{1}{u_j^*} \frac{\delta E_c^{(n)}}{\delta u_j}. \quad (38)$$

In the next section we will show that the functional derivation with respect to the orbitals can be given analytically and finally one can get closed form for the correlation potential at  $n$ th-order level of PT.

According to Eqs. (22-26) the following self-consistent Kohn-Sham procedure can then be constructed, which is correlated at the  $n$ th order level of RS PT,

$$\begin{aligned} [-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_x(\mathbf{r}) + v_c^{(n)}(\mathbf{r})]u_i(\mathbf{r}) \\ = \epsilon_i u_i(\mathbf{r}). \end{aligned} \quad (39)$$

We will discuss the various properties of this self-consistent KS PT scheme in section V.

#### IV. THE CORRELATION ENERGY AND POTENTIAL AT SECOND ORDER

Because of the increasing complexity of perturbation expansion, we give here only the MP perturbation energy at second order. For a general case one can give (in principle) those quantities at higher order as well. Note that one has to consider not only *double* excitations but also *single* configurations. In case of HF theory  $E_c^{(2),single} = 0$  by Brillouin theorem, but in case of KS self-consistent orbitals we still have to calculate it [30–32]. This term does not vanish completely but must be rather small for KS orbitals as well. For a closed-shell system, the second-order energy can be written in terms of sums over spatial orbitals as

$$\begin{aligned} E_c^{(2)}[\{u_i\}] &= E_c^{2,single} + E_c^{2,D} \\ &= \sum_{r=1}^2 \frac{|\langle \Phi_s | \hat{V}_{ee}(\mathbf{r}) - \hat{v}^{OEP}(\mathbf{r}) | \Phi_{s,r} \rangle|^2}{E_s - E_{s,r}} \\ &= \sum_i^{occ} \sum_k^{vir} \frac{|\mathbf{W}_{ik}|^2}{\epsilon_i - \epsilon_k} + \sum_{ij}^{occ} \sum_{kl}^{vir} \frac{|\mathbf{W}_{ij}^{kl}|^2}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l}. \end{aligned} \quad (40)$$

$$\mathbf{W}_{ik} = \langle \Phi_s | \hat{\mathbf{W}} | \Phi_i^k \rangle = - \sum_j \langle ij | ik \rangle - \bar{v}_{x,ik}^{OEP},$$

$$\bar{v}_{x,ik}^{OEP} = \langle i | v_x^{OEP}(\mathbf{r}) | k \rangle,$$

$$\mathbf{W}_{ij}^{kl} = \langle \Phi_s | \hat{\mathbf{V}}_{ee} | \Phi_{ij}^{kl} \rangle = |\langle ij || kl \rangle|^2, \quad (41)$$

where  $|\langle ij||kl\rangle|^2 = \langle ij|kl\rangle(2\langle kl|ij\rangle - \langle kl|ji\rangle)$ ,

$$\langle ij|kl\rangle = \int d\mathbf{r}d\mathbf{r}' \frac{u_i(\mathbf{r})u_j(\mathbf{r}')u_k(\mathbf{r})u_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (42)$$

$\Phi_s$  is the  $N$ -electron Kohn-Sham ground-state single determinant wave function. The  $r$ th excited state to the Kohn-Sham equation is given by  $\Phi_{s,r}$ . The expectation values are as follows,  $E_s = \langle \Phi_s | \hat{H}_0 | \Phi_s \rangle$  and  $E_{s,r} = \langle \Phi_{s,r} | \hat{H} | \Phi_{s,r} \rangle$ . Note that since the quantity being summed in Eq. (42) is symmetric in  $i, j, k$  and  $l$  it vanishes when  $i = j$  or  $k = l$ .

The next question to be addressed is the derivation of the correlation potential  $v_c$  according to Eqs. (15) and (18) bearing in mind the decomposition  $v_{xc} = v_x + v_c$ . The correlation potential at a given order of the perturbation series  $v_c^{(n)}(\mathbf{r})$  can be given formally by means of a functional derivative of the correlation energy  $E_c^{(n)}$  with respect to the orbitals  $u_i(\mathbf{r})$  according to Eqs. (13) and (38) via the orbital dependent quantity

$$\begin{aligned} v_{ci}^{(2)}(\mathbf{r}) &= \frac{1}{u_i^*(\mathbf{r})} \frac{\delta E_c^{(2)}[\{u_i\}]}{\delta u_i(\mathbf{r})} \\ &= \frac{1}{u_i^*(\mathbf{r})} \left\{ \frac{\delta E_c^{(2),single}}{\delta u_i(\mathbf{r})} + \frac{\delta E_c^{(2),D}}{\delta u_i(\mathbf{r})} \right\}. \end{aligned} \quad (43)$$

According to Eqs. (38) and (41) the quantity  $v_{ci}^{(n)}$  at second order

$$\begin{aligned} v_{ci}^{(2)}(\mathbf{r}) &= v_{ci}^{(2),single} + v_{ci}^{(2),D} = \\ &= -\frac{2}{u_i^*} \left\{ \sum_k^{vir} \frac{\sum_j^{occ} ([j|ik] + [ij|k]) + [v_x^{OEP}k] + [ik \frac{\delta v_x^{OEP}}{\delta u_i}]}{\epsilon_i - \epsilon_k} \right. \\ &\quad \left. + \sum_j^{occ} \sum_{k>l}^{vir} \frac{[j|kl]^2}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l} \right\}, \end{aligned} \quad (44)$$

since

$$[j|kl]^2 = \frac{\delta}{\delta u_i(\mathbf{r})} |\langle ij||kl\rangle|^2 = [j|kl](2\langle kl|ij\rangle - \langle kl|ji\rangle) + [kl|j]\langle ij|kl\rangle \quad (45)$$

$$[j|kl] = u_k(\mathbf{r}) \int d\mathbf{r}' \frac{u_j(\mathbf{r}')u_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$

The Slater component of the second order correlation potential given by Eq. (35) will be precisely

$$v_c^{S,(2)}(\mathbf{r}) = v_c^{S,single,(2)}(\mathbf{r}) + v_c^{S,D,(2)}(\mathbf{r}). \quad (46)$$

Using the decomposition  $v_{xc} = v_{xc}^S + v_{xc}^{resp}$ , the potential part of  $v_{xc}$  or equivalently the generalized Slater component of Eq. (18) at second order of PT can be finally written (note that only *double* excitations are included,  $v_c^{single,(2)}$  is given in the Appendix),

$$\begin{aligned} v_{xc}^{S,D,(2)}([\rho, \{u_i, \epsilon_i\}]; \mathbf{r}) &= v_x^S(\mathbf{r}) + v_c^{S,D,(2)}(\mathbf{r}) = \\ &= \frac{1}{\rho} \left( \sum_{ijkl}^{occ} [ij|kl] + \sum_{ij}^{occ} \sum_{kl}^{vir} \frac{[ij|kl]^2}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l} \right), \end{aligned} \quad (47)$$

and the generalized response part

$$\begin{aligned} v_{xc}^{resp,D,(2)}([\rho, \{u_i, \epsilon_i\}]; \mathbf{r}) &= v_x^{resp}(\mathbf{r}) + v_c^{resp,D,(2)}(\mathbf{r}) = \\ &= \sum_{ij}^{m-1} \frac{\rho_i}{\rho} \mathbf{A}_{ij}^{-1} \left\{ \sum_{ikl}^{occ} \int d\mathbf{r} \frac{\rho_j}{\rho} \sum_j^{occ} [ij|kl] - \frac{1}{4} \langle ij|kl \rangle + \right. \\ &\quad \left. \sum_i^{occ} \sum_{kl}^{vir} \left( \int d\mathbf{r} \frac{\rho_j}{\rho} \sum_j^{occ} \frac{[ij|kl]^2}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l} - \frac{|\langle ij||kl\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l} \right) \right\}. \end{aligned} \quad (48)$$

The expression is given only up to the second order, and the extension of the formula to include higher order terms is straightforward, although order-by-order with increasing complexity [30].

## V. THE SELF-CONSISTENT PERTURBATION SCHEME

Having discussed the partition scheme and the formulation of  $n$ th-order xc-potential, we would like to study the procedure given by Eq. (39). This scheme allows one to improve the eigenfunctions and eigenvalues of the unperturbed problem systematically. The  $n$ th-order correlation potential  $v_c^{(n)}(\mathbf{r})$  (Eq. (33)), which is calculated on top of the first-order level of perturbation theory, is substituted back to the exchange-only KS equation in order to achieve self-consistency in the field of  $v_c^{(n)}$ . The introduction of  $v_c^{(n)}$  via Eq. (33) together with Eq. (39) opens a new variational freedom in the original KS Eq. (2), which leads to a new iterative scheme. A new  $v_c^{(n)}$  can then also be constructed on top of the variationally solved correlated KS-problem, however, this would lead to a more complicated iterative scheme.

The iterative scheme given by Eq. (39) is working in the following way:

(i) one has to solve the first order level of theory which is exactly the exchange-only OEP reference state in this particular case providing the set of orbitals and eigenvalues,  $\{u_i\}$  and  $\{\epsilon_i\}$ .

(ii) the next step is the construction of the  $n$ th-order correlation energy (Eq. (31)) and the exchange-correlation potential  $v_{xc}^{(n)}$  on top of the exchange-only reference state (Eqs. (18) and (33)).

(iii) substituting back the potential  $v_c^{(n)}$  obtained in step (ii) to the KS equation a new correlated KS problem can be solved. In this way a new set of eigensolution  $\{u_i, \epsilon_i\}$  can be obtained. One can stop at this point, when the  $n$ th-order correlated KS problem is solved, and

the ground state energy can then be calculated by Eq. (9).

(iv) Although present paper is addressed to the formulation of a standard perturbation theory on top of x-only OEP (steps i-iii), we indicate that further iterative steps can also be considered in practice when  $n \neq \infty$ . The orbitals  $\{u_i\}$  and the potential  $v_x$  obtained in step (iii) differ from those obtained in step (i). Therefore, a new  $E_c^{(n)}$  and  $v_c^{(n)}$  can be calculated which, however, leads to a KS problem again. This procedure continues until convergency is reached, provided, of course, that such a method turns out to be convergent. These additional iterative steps with the "updated"  $v_c^{(n)}$  result, however, in the change of the unperturbed problem. This would lead to the change of the partition scheme, the formula given by Eq. (40) for  $E_c^{(n)}$  e.g. at second order of PT. Therefore, in Eq. (40)  $v^{OEP}(\mathbf{r})$  contains not only  $v_x$  but also  $v_c^{(2)}(\mathbf{r})$  so that,

$$\hat{W}^{(2)}(\mathbf{r}) = \hat{V}_{ee}(\mathbf{r}) - \hat{v}^{OEP}(\mathbf{r}) + v_c^{(2)}(\mathbf{r}). \quad (49)$$

Here we restrict ourself to the discussion of iterative procedure with only unchanged partition scheme of the Hamiltonian. The more comprehensive discussion of such a RS scheme with improved partition of the Hamiltonian can be the subject of further studies.

The solutions of the correlated KS equation obtained in step (iii) can only be taken as final solutions of Eq. (39) when infinite order PT is employed for calculating  $v_c^{(n)}$  ( $n = \infty$ ). This is because the RS theory is mathematically equivalent representation of the full configuration interaction (full CI) theory [30] at infinite order expansion. In practice, only truncated perturbation expansions can only be considered, and, as such, fast convergence in the PT expansion is of great importance. Therefore, the proper choice of the reference space is also important to achieve rapid convergence [34]. Note that in this scheme the reference state is subsequently optimized when steps (i)-(iv) are used.

Like in standard Hartree-Fock or KS procedures, the single particle Eq. (39) have to be solved iteratively until self-consistency is reached. According to Eq. (33) the scheme can be improved systematically by considering higher order  $v_c^{(n)}$ . One of the main differences between the original form of the RS scheme and which is given in Eq. (39) is that in the OEP PT scheme the wave-function and the eigenvalues are improved via the solution of the  $n$ th-order KS problem. This theory never goes beyond the single-determinant picture in the present form. Excited configurations are considered, however, when calculating  $E_c^{(n)}$  and  $v_c^{(n)}$ . This scheme allows one to drive a system progressively from a noninteracting reference state toward a fully correlated system. When step (iv) is switched on, the orbitals  $\{u_i\}$  and eigenvalues  $\{\epsilon_i\}$  in the RS expansion of  $E_c^{(n)}$  (Eq. (31)) are allowed to be the updated ones in the RS perturbation expansion. The scheme can therefore be considered as a *self-consistent*

RS perturbation problem (SC-RS OEP). An alternative approach to carry out PT calculation self-consistently is the variation-perturbation approach [18,34]. Within the exact SC-RS OEP scheme self-consistency can be reached once the exact  $v_{xc}$  is evaluated. We hope that this iterative scheme might have the "charming feature" of including the important part of electron correlation already at the second order of the correlation energy. Normally, the eigenvalue problem up to the first order level of theory is solved variationally. The iterative scheme (39) permits getting the best optimized first order reference state in RS theory. The optimization of the reference state is accomplished by the reiteration of the updated xc-potential and by the consequent solutions of the "updated" KS problems until convergency is reached in step (iv). The self-consistent scheme given by Eq. (39) is similar to the so-called density functional perturbation theory (DFPT) [18] in that respect that successive orders of perturbation are obtained iteratively in both cases. However, DFPT uses energy derivatives with respect to the ordering parameters as a variation-perturbation treatment.

Görling and Levy (GL) [11,28] have given more general functional for  $E_{xc}$  and for  $v_{xc}$  on the basis of PT. They found on KS basis that both the xc-energy and the xc-potential must be complicated functionals of both orbitals and eigenvalues and also of a linear response function type inverse operator  $\hat{G}^{-1}$ . However, the quantity  $\hat{G}^{-1}$  is analytically unknown. The GL perturbation theory can provide an exact formal Kohn-Sham scheme only in basis set representation. Both the GL and the OEP PT theories lead to the exact formal representation of the KS equation, however, the construction of the  $n$ th-order  $v_{xc}$  is different. In the GL PT a coupling constant  $\alpha$  dependent scheme links the noninteracting  $N$ -electron system with the interacting real system where the electron density remains independent of  $\alpha$  [28]. The correlation potential and the energy are expressed in a Taylor series with respect to the  $\alpha$ . The OEP PT scheme is a coupling-constant free formalism and the electron density does not remain constant during the perturbation treatment. The exchange-only OEP will result in different density from Eq. (39), although the difference may be rather small. In OEP PT a particular form of  $v_{xc}$  is used given by Eq. (15), while in GL PT a more general, but unknown form of  $v_{xc}$  is used. The main advantage of the present scheme is that the functional derivative Eq. (38) is directly accessible and, therefore, the  $n$ th-order potential  $v_c^{(n)}$  can be given analytically. Both theories deliver the exact exchange-correlation energy and potential order by order. Holas and March give the leading term of GL PT correlation potential in terms of first and second order density matrixes (2DM). The 2DM is also expressed by PT. They also derived an exchange-potential which is free of the energy denominators  $\epsilon_i - \epsilon_k$  while the corresponding expression in GL theory does contain it [19]. The extension of relativistic exchange-only OEP with perturbation theory has first been suggested by Engel *et al.* very recently [15]. Although their scheme is



closely related to our OEP-PT approach, the construction of the correlation potential seems to be somewhat different. Not taking into account its relativistic features functional derivatives appear in their approach with respect to the eigenvalues which are not included in the present scheme. We use Eq. (33) for the correlation potential together with Eq. (38) which will lead to somewhat different formula than that given by Engel *et al.*. Although they give a very accurate and detailed formulation of the theory we believe that our approach is still relevant for applications in the next future.

In our SC OEP PT scheme the exchange-correlation potential can be given according to OEP method. The most convenient way is to use the KLI approximation [3] for the xc-potential according to Eq. (18). The exchange-only KLI approximation given by Eq. (18) performs remarkably well [3,14] providing nice agreement with the Hartree-Fock total energies. In the GL scheme one has a relatively complicated formula at the first order level of PT, e.g. at the exchange-only level using orbital, eigenvalue and  $\hat{G}^{-1}$  dependent exchange-potential. The SC OEP-PT method uses the much simpler exchange potential according to Eqs. (15) and (29) which is only orbital-functional. However, the OEP PT scheme given in Eq. (39) leads to completely exact theory when the last term in Eq. (15), which is neglected in the KLI approximation, is calculated as well. Although the integrodifferential equation Eq. (12) can be solved only numerically, however, its exact transformation given by Eq. (15) can be computed exactly for arbitrary fermionic system. The neglected term in Eq. (15), when considered, can increase the computational difficulties significantly.

$E_{xc}^{(n)}$  is also the functional of the optimized exchange-correlation potential  $v_{xc}^{(n)}$  via the iterative scheme given by Eq. (39),

$$E_{xc}^{(n)} = E_{xc}^{(n)}[\{\Phi_s\}, \{\epsilon_i\}, v_{xc}^{(n)}]. \quad (50)$$

This is because in steps (iii) and (iv) in Eq. (39) the correlated KS problem is solved using the "updated"  $v_c^{(n)}$ . This equation reflects the complexity of the eigenvalue problem given by Eq. (38). Also, Eq. (50) demonstrates the difference of the SC-RS OEP scheme from the original formulation of the RS perturbation theory. The expanded  $n$ th order correlation energy is explicit functional not only of the self-consistent orbitals and the eigenvalues, but also of the self-consistent exchange-correlation potential. Similar results are reported on Sham-Schlüter basis [13,14] and by Engel *et al.* [15]. In that and other studies the variational energy expression has been treated as the functional of the fully dressed Green function  $G$  and of the reference function  $G_0$ , and they are associated with the Dyson equation [12].

## VI. CONCLUSIONS

In this paper we have introduced a first-principle, parameter-free perturbational density functional scheme in which all exchange-correlation effects are consistently represented in terms of the eigensolutions of the Kohn-Sham equations. A self-consistent formulation of perturbation theory is developed on top of the exchange-only optimized effective potential (OEP) method. This generalization of OEP opens a new variational freedom which leads to a new iterative procedure. The total energy is also the functional of the  $n$ th-order exchange-correlation potential. In this scheme, the correlation energy and the correlation potential is expressed via perturbation series while the orbitals and the eigenvalues are variationally optimized via the Kohn-Sham equation. We give exactly the potential and the response parts of the exchange-correlation potential which are explicitly functionals of the eigensolutions of the Kohn-Sham eigenvalue problem. The correlation potential is given directly as a functional derivative over the Møller-Plesset correlation energy expression with respect to the Kohn-Sham orbitals.

We also discuss the difference and similarities between the present and other perturbation theories which are also based on Kohn-Sham orbitals.

Further investigations will be fruitful starting from the formalism introduced concerning the selection of the most appropriate reference state, the Hamiltonian partition scheme and the convergence of the RS PT based on OEP. We would like to emphasize the utility of Eq. (39) as a way of improving Kohn-Sham eigenvalues for calculations of band gaps, ionization potentials and excitation energies. The self-consistent OEP PT scheme introduced here can be useful in a wide range of areas in quantum chemistry and in solid state physics. Whether the present approach can be really competitive among known high accuracy but costly approaches, such as configuration interaction (CI), will be hopefully the subject of further tests in the future.

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## APPENDIX

In order to get the second-order correlation potential one has to derive the single excitation components which occur when we are dealing with a "one-body" single particle Hamiltonian. In Hartree-Fock theory single particle

excitations do not play a role in the second order PT correlation energy formula because  $\langle \Phi_s | \hat{W} | \Phi_s^{ik} \rangle = 0$  where  $\Phi_s^{ik}$  is the single excited determinant wave function. However, its magnitude and contribution to the second-order correlation energy in PT-DFT must be rather small as well. Further arguments in this respect can be given only computationally.

Let us again decompose  $v_c^{(2)}$  into contributions from *single* and *double* excitations,

$$v_c^{(2)}(\mathbf{r}) = v_c^{single,(2)}(\mathbf{r}) + v_c^{D,(2)}(\mathbf{r}). \quad (51)$$

$v_c^{D,(2)}$  has been given already in section IV in Eqs. (47) and (48). Together with Eqs. (33)-(38)  $v_c^{single,(2)}$  can be partitioned to Slater and response parts

$$v_c^{single,(2)} = v_c^{S,single,(2)} + v_c^{resp,single,(2)}, \quad (52)$$

$$v_{ci}^{(2),single} = \frac{1}{u_i^*} \frac{\delta E_c^{(2),single}}{\delta u_i}, \quad (53)$$

where

$$\frac{\delta E_c^{(2),single}}{\delta u_i} = -2 \sum_k^{vir} \frac{\sum_j^{occ} ([j|ik] + [ij|k]) + \frac{\delta \bar{v}_{x,ik}^{OEP}}{\delta u_i}}{\epsilon_i - \epsilon_k}. \quad (54)$$

$$\bar{v}_{x,ik}^{OEP} = \langle i | v_x^{OEP}(\mathbf{r}) | k \rangle, \quad (55)$$

$$\frac{\delta \bar{v}_{x,ik}^{OEP}}{\delta u_i} = \frac{\delta \bar{v}_{x,ik}^S}{\delta u_i} + \frac{\delta \bar{v}_{x,ik}^{resp}}{\delta u_i}, \quad (56)$$

$$\frac{\delta \bar{v}_{x,ik}^S}{\delta u_i} = v_x^S(\mathbf{r}) u_k(\mathbf{r}) + u_i(\mathbf{r}) u_k(\mathbf{r}) \frac{\delta v_x^S}{\delta u_i}, \quad (57)$$

$$\frac{\delta v_x^S}{\delta u_i} = \frac{1}{\rho} \left( \frac{u_i^* e_x^{HF}}{\rho} - \frac{\delta e_x^{HF}}{\delta u_i} \right) \quad (58)$$

where formally the HF exchange energy density is the one given in Eq. (29) e.g.,

$$E_x^{OEP} = \int d\mathbf{r} e_x^{HF} [\{u_i^{OEP}(\mathbf{r})\}], \quad (59)$$

$$e_x^{HF} = v_x^S(\mathbf{r}) \rho(\mathbf{r}). \quad (60)$$

$$\frac{\delta \bar{v}_{x,ik}^{resp}}{\delta u_i} = v_x^{resp}(\mathbf{r}) u_k(\mathbf{r}) + u_i(\mathbf{r}) u_k(\mathbf{r}) \frac{\delta v_x^{resp}}{\delta u_i}, \quad (61)$$

$$\begin{aligned} \frac{\delta v_x^{resp}}{\delta u_i} &= \frac{\rho_i}{\rho} \sum_{j=1}^{m-1} \left[ \frac{\delta \mathbf{A}_{ij}^{-1}}{\delta u_i} (\bar{v}_{xj}^S - \bar{v}_{xj}^{HF}) \right. \\ &\quad \left. + \mathbf{A}_{ij}^{-1} \left( \frac{\delta \bar{v}_{xj}^S}{\delta u_i} - \frac{\delta \bar{v}_{xj}^{HF}}{\delta u_i} \right) \right] \\ &\quad + \frac{u_i^*}{\rho} \sum_{j=1}^{m-1} \mathbf{A}_{ij}^{-1} (\bar{v}_{xj}^S - \bar{v}_{xj}^{HF}), \end{aligned} \quad (62)$$

$$\frac{\delta \bar{v}_{xj}^S}{\delta u_i} = \left( \frac{\delta e_x^{HF}}{\delta u_i} \rho - e_x^{HF} u_i^* \right) \rho^{-2} \rho_j. \quad (63)$$

The functional derivative over the HF exchange energy density

$$\frac{\delta e_x^{HF}}{\delta u_i} = -\frac{1}{4} \sum_{j=1}^{occ} \int d\mathbf{r}' \frac{u_i^*(\mathbf{r}') u_j(\mathbf{r}) u_j^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (64)$$

For the inverse matrix  $\mathbf{A}_{ij}^{-1}$  the following equality holds,

$$\frac{\delta \mathbf{A}_{ij}^{-1}}{\delta u_i} = \sum_{j=1}^{m-1} \mathbf{A}_{ij}^{-1} \frac{\delta \mathbf{A}_{ij}}{\delta u_i} \mathbf{A}_{ij}^{-1}, \quad (65)$$

where

$$\frac{\delta \mathbf{A}_{ij}}{\delta u_i} = -\frac{u_i^* \rho_j}{\rho^2} (1 - \rho_i). \quad (66)$$

For simplicity, we give here the terms in conjunction with the remarkable KLI approximation [3], therefore the last term given in Eq. (15) is neglected. However, this term is rather small [3,14] and can be accounted for when high numerical accuracy is required.

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